Raman measurements of heavy ion irradiated water-bearing minerals*

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Our research was triggered by the question if crystal water of natural minerals is released during irradiation with swift heavy ions. To answer this question natural microcrystalline malachite ($Cu_2[(OH)_2/CO_3]$) and gypsum ($CaSO_4*2H_2O$) were irradiated at the UNILAC (GSI) with 11.1 MeV/u ^{209}Bi-ions applying fluences between 1×10^6 – 2×10^{12} ions/cm^2. All crystals were analyzed by Raman spectroscopy using the LabRam HR800 UV spectrometer equipped with an OLYMPUS BXFM-ILHS optical microscope, a grating with 1800 grooves per millimeter, a Peltier-cooled CCD detector, and an objective of 50x magnification. For excitation, a blue laser with a wavelength of 473.03 nm was used. The lateral resolution was ~2 µm, the wave number accuracy 0.5 cm^{-1}, and the spectral resolution 1 cm^{-1}.

Malachite and gypsum are both anisotropic crystals, have a monoclinic structure and two optical axes. Malachite has variable crystallographic orientations and growth directions and consequently the intensities of the different malachite bands vary. This variation is demonstrated in Fig. 1 for spectra recorded under different crystallographic directions and cleaving planes.

For irradiated gypsum, significant changes in the Raman spectra appear above a fluence of 1×10^{10} Bi-ions/cm². With increasing fluences the intensity of most Raman bands decreases. This applies especially to the

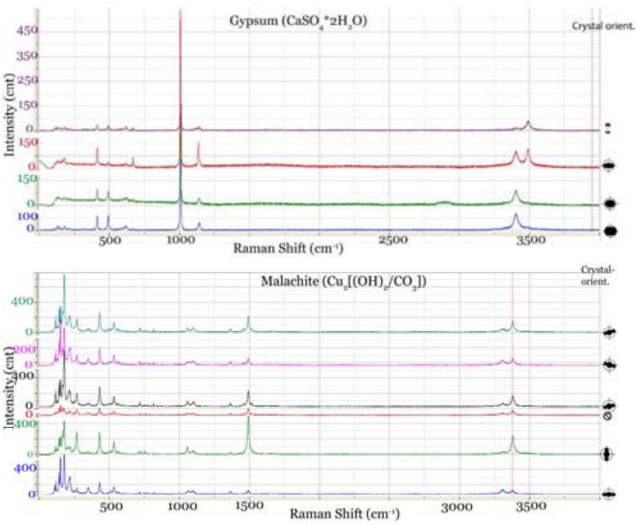

Fig. 1: Raman spectra of gypsum (top) and malachite (bottom) at different crystal orientations.

υ_1 stretching mode at 3404 cm^{-1} and the υ_3 stretching mode at 3492 cm^{-1}, which characterize the H_2O bands. The decrease of amplitudes is an indication of irradiation-induced release of water. Although the lattice water is set free, the mineral is not transformed to anhydrite ($CaSO_4$), which is the waterless sulfate. The bands remain at their characteristic gypsum position and do not shift to the anhydrite position.

Also for malachite the amplitude of different Raman bands decrease with increasing fluence. In contrast to the Raman bands of gypsum, the OH stretching vibration modes at 3308 and 3380 cm^{-1} of malachite are equal sensitive than the other bands. Significant changes in the spectra as well as discoloration of the crystal (Fig. 2) also appear above a fluence of 1×10^{10} Bi-ions/cm². The color change from green to black indicates a phase transformation of the irradiated layer showing Raman bands at ~1360 cm^{-1} and ~1580 cm^{-1}, typical for graphite. Under irradiation, the band positions in the malachite spectra slightly change but not systematically.

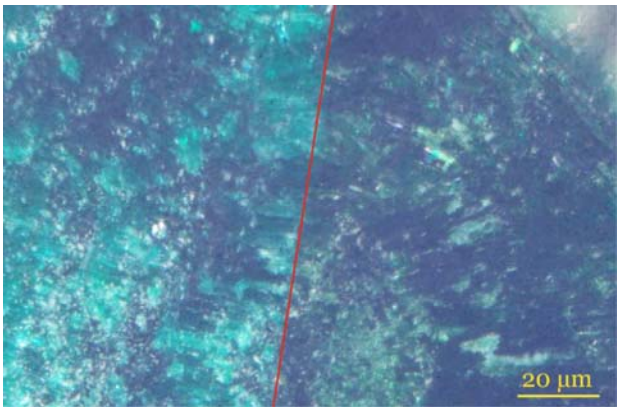

Fig. 2: Malachite sample showing the beginning of discoloration at a fluence of 1×10^{10} Bi-ions/cm² at the right site of the red line. The left side of the crystal is non-irradiated for comparison.

References

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*Work supported by HGS-HIRe
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DOI:10.15120/GR-2015-1-APPA-MML-MR-12